

Ammonium Sulfate WFGD Technology
OVERVIEW FOR GENERAL INDUSTRY INFORMATION
July 2007

Background

Marsulex Environmental Technologies (MET) has developed an effective ammonia scrubbing technology that removes sulfur dioxide (SO₂) from boiler flue gases and produces high-value ammonium sulfate (AS) fertilizer. The AS scrubbing system uses proven wet flue gas desulfurization (WFGD) equipment and therefore can achieve the same high reliability of the more traditional limestone-based WFGD. The produced high-value AS fertilizer enhances the project economics.

The first field pilot of this technology was successfully executed at the Dakota Gasification (DGC) facility in the early 1990's and led to a subsequent full-scale commercial installation at that site. This AS WFGD system has been scrubbing flue gas and producing fertilizer in accordance with design for well over 10 years now. In late 2006, the second commercial application of the AS WFGD went into operation at the Syncrude Upgrading Expansion – Phase 1 (UE-1) Project in Alberta, Canada.

The MET AS WFGD process is similar to the more familiar limestone/gypsum WFGD process as illustrated in Figure 1. In fact, many components are common between these two processes, such as the absorber vessel, recycle pumps, spray nozzles, etc. The equipment components which differ are reagent handling and dewatering. Limestone-based WFGD usually requires a fairly complex reagent slurry preparation system consisting of a limestone storage silo, weigh feeder, wet ball mill with all required accessory equipment, cyclone classifier, ball mill product sump with agitator, ball mill product pumps, limestone slurry tank and limestone slurry feed pumps. In comparison, the simpler AS WFGD ammonia feed system consists of an ammonia storage tank, ammonia feed pumps and a vaporizer in the event of anhydrous ammonia supply. The AS WFGD process employs centrifuges for dewatering, in lieu of belt or rotary drum filters, based on their ability to produce a low moisture cake and smaller plot area requirement.

Economics

The favorable economics of the MET AS-FGD technology resides in the ability to process low cost, high sulfur coals while generating a high-value fertilizer product. The economic model of the AS-FGD favors higher sulfur in the fuel via the increased AS production rate and potential for higher net

revenues to the plant if fuel cost savings can be realized. The potential revenues from the fertilizer product can potentially off-set the operating cost of the absorber system and contribute to capital recovery charges depending on the market for ammonium sulfate fertilizer and the cost of ammonia.

Capital recovery periods due to AS sales/fuel savings as well as future AS sales revenues are subject to:

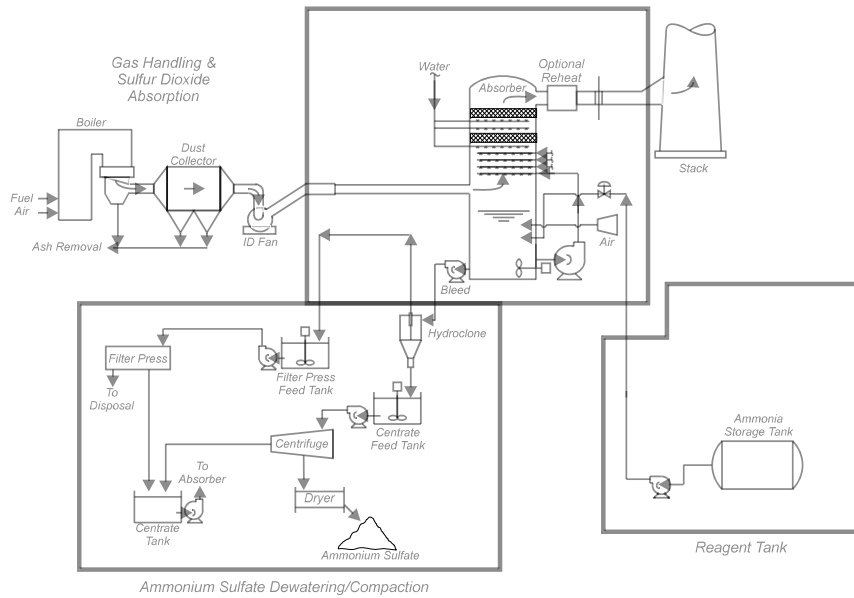
- Regional pricing/capacity for AS produced
- Sourcing/cost of ammonia
- Availability/cost of higher sulfur fuels
- Plant capacity factors
- Incremental capital differential over competing alternative
- Plant life cycle and internal cost of capital rates

Process Description

In the patented, Marsulex Ammonium Sulfate process, SO₂ scrubbing is accomplished using a saturated solution of ammonium sulfate in a spray tower absorber. Anhydrous or aqueous ammonia is fed into the absorber recirculation tank under pH control as the reagent for SO₂ absorption. Primary reaction products of ammonium sulfite / bisulfite are converted to ammonium sulfate through forced oxidation in the absorber recycle tank. Using the thermal energy of the flue gas, a portion of the byproduct ammonium sulfate is continually crystallized from the saturated absorber liquor forming a suspension of ammonium sulfate. By maintaining high recirculation of absorbing liquor and a relatively low pH, ammonia slip in the outlet flue gas is kept at low levels which avoids the plume visibility problem that has been a stumbling block of previous ammonia scrubbing processes.

A product bleed stream from the absorber is first dewatered in a set of hydroclones followed by a centrifuge to generate an ammonium sulfate product cake of approximately 98%+ solids. All the recovered solution is recycled to the absorber. The centrifuge cake is further processed in a dryer/cooler and subsequent compaction granulator to make final ammonium sulfate product with < 0.5% moisture content. The dried ammonium sulfate granules are then stored and shipped for sale.

Ammonium Sulfate Process



Limestone/Gypsum Process

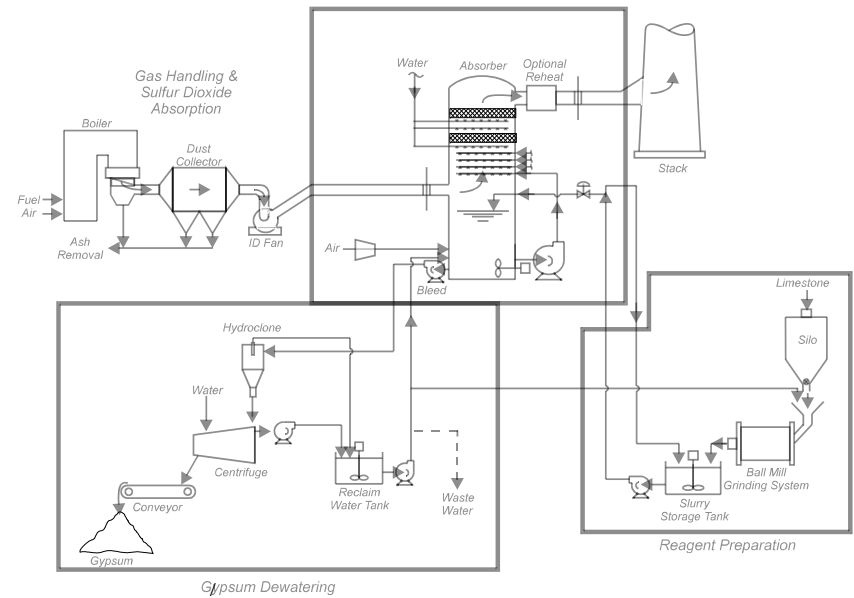


Figure 1 – Ammonia and Limestone WFGD Process Comparison

The patented MET ammonium sulfate scrubbing process in Figure 1 produces high-value fertilizer while providing equivalent or better SO₂ removal efficiency as compared to the more conventional limestone/gypsum scrubbing process. The improved SO₂ removal efficiency of the AS WFGD relative to limestone WFGD over a range of fuel % sulfur content for a constant liquid-to-gas ratio (L/G) is illustrated in Figure 2. This advantage of the ammonia system due to the water soluble chemistry improves with increasing fuel % sulfur content.

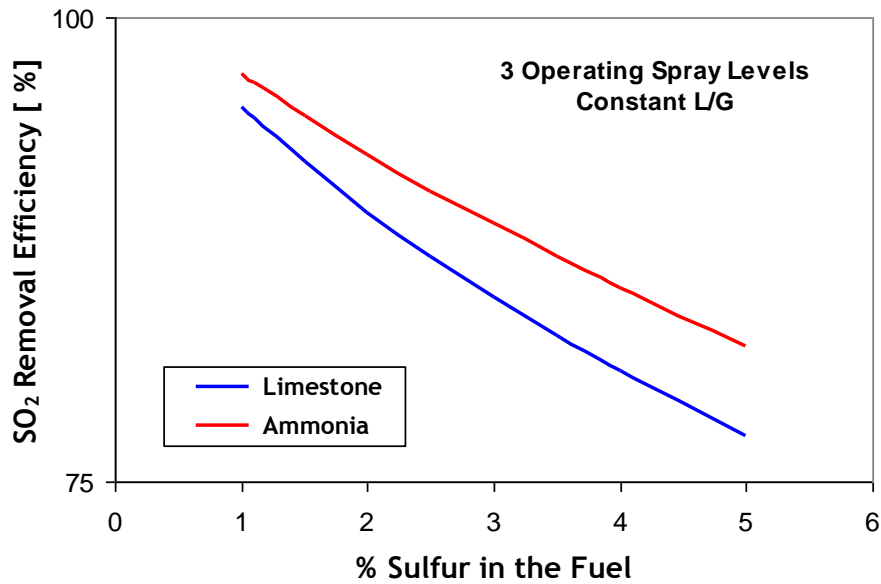
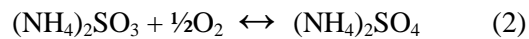
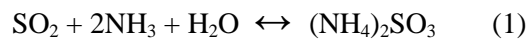


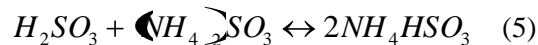
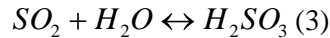
Figure 2 – Impact of Fuel %S on SO₂ Removal for Ammonia versus Limestone

Process Chemistry

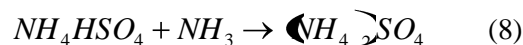
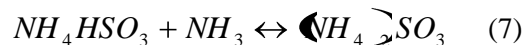
The chemistry of the AS WFGD is similar to the chemistry using a limestone reagent in that the major steps are absorption and oxidation. The overall reactions which occur in the MET AS absorber are as follows:



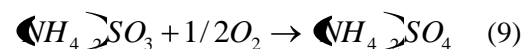
The actual chemical mechanism is more complex and involves sulfite-bisulfite and sulfate-bisulfate reactions:



SO₂ in the flue gas first comes into contact with spray droplets of aqueous slurry. In reaction (3), SO₂ from the flue gas dissolves in the water to form sulfurous acid. In reactions (4) and (5), the sulfurous acid reacts further with dissolved ammonium sulfate and sulfite salts in the solution to form intermediate acidic species. The formation of the sulfurous acid, including the acidic species, lowers the pH of the slurry.



The ammonia added to the process in reactions (6) to (8) neutralizes the acidic species to ammonium sulfite and ammonium sulfate. This neutralization serves to restore the pH to its desired value.



Oxidation air injected into the absorber tank in reaction (9) oxidizes the remaining ammonium sulfite to ammonium sulfate.



The resulting ammonium sulfate solution is saturated and ammonium sulfate crystals, in reaction (10), precipitate from the solution due to chemical reaction and water evaporation into the flue gas. The heat of evaporation is supplied by the residual heat in the flue gas. Nitrogen content of the product is approximately 21% weight while sulfur content is approximately 24%.weight. When applied to soils, the sulfur constituent of the ammonium sulfate acts as a catalyst which increases the rate of nitrogen uptake by various crops.

Advantages of the Marsulex Ammonium Sulfate System

The system is designed with standard conventional critical equipment redundancy similar to that of limestone based systems. This similarity upstream of the centrifuge allows flexibility to operate the flue gas desulfurization system with either limestone or ammonia as a reagent.

Additionally, the water soluble chemistry of ammonium sulfate prevents any type of internal solids buildup as opposed to that potential with limestone scrubbing. Ammonia, being more reactive than limestone, is capable of achieving sustainable, high 98%+ removal efficiencies at extremely high fuel sulfur contents.

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